

PATENT ABSTRACTS OF JAPAN

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(54) PARTIAL PLATING METHOD AND RESIN MEMBER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a partial plating method in which roughening treatment is unnecessary and excellent pattern adhesion is attained.

SOLUTION: The partial plating method comprises steps of: allowing a plating-inducing substance to adhere into a state of desired pattern to the surface of a molded body of a curable resin composition (step A); curing the molded body of the curable resin composition, which is passed through the step A, to prepare a resin basis material having an initiator pattern composed of the plating-inducing substance (step B); and applying electroless plating to the pattern (step C).

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CLAIMS

[Claim(s)]

[Claim 1] The partial plating approach which consists of what the resin base material which has the initiator pattern which consists of a plating inducer by hardening the Plastic solid of the hardenability resin constituent which passed through Process A after making a plating inducer adhere to the front face of the Plastic solid of a hardenability resin constituent in the shape of [desired] a pattern (process A) is obtained (process B), and nonelectrolytic plating is performed for subsequently to the pattern top concerned (process C).

[Claim 2] The partial plating approach according to claim 1 which is what a plating inducer becomes from the compound which has metal coordination ability.

[Claim 3] The partial plating approach according to claim 1 which is that to which hardening in Process B is performed by heat.

[Claim 4] The partial plating approach according to claim 1 (process B') which oxidizes a resin base material front face before Process C.

[Claim 5] The partial plating approach according to claim 1 of having the process (process D) which heats a resin base material after Process C.

[Claim 6] The resin member which has the metal pattern formed by one approach of claims 1-5.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the partial plating approach for forming a metal pattern in a resin base material front face.

[0002]

[Description of the Prior Art] The resin member which has a metal detailed line (metal pattern) on a resin base material (it may only be hereafter called base material) front face is used for a semiconductor

device, semiconductor device mounting components, various panel indicating equipments, the IC card, and the optical device. It is common that formation of such a metal detailed line (metal pattern) is performed by plating. It is divided into the approach of galvanizing to the shape of a pattern of the request of nonelectrolytic plating to the approach of growing up a metal with electrolysis plating through the mask pattern after dividing roughly the metal pattern formation approach by plating and performing nonelectrolytic plating all over a resin base material, and removing nonelectrolytic plating unnecessary subsequently, and a resin base material (partial plating), forming a direct metal pattern, and growing up plating on it if needed. When the metallic corrosion by the chemical used in case unnecessary nonelectrolytic plating is removed does not arise, since the nonelectrolytic plating clearance process is unnecessary, the approach of the latter using partial plating is excellent in productivity.

[0003] If the initiator pattern (it is also called the coat for nonelectrolytic plating) which consists of a plating inducer is formed in a resin base material front face on the occasion of partial plating and it galvanizes on this pattern, it is known that a metal pattern will be obtained easily (JP,7-263841,A etc.). About the plating inducer, many examination aiming at the adhesion to a resin base material or amelioration of a pattern configuration is made. The conductive ingredient which consists of mixture with a conductive polymer or its precursor, water, or polar solvents as an example of a plating inducer (JP,2002-26014,A), the constituent (JP,7-131135,A --) which consists of a fusibility palladium salt, a water-soluble solvent, and water JP,7-245467,A, the ingredient containing a photosensitive palladium macromolecule chelate compound (JP,2000-147762,A), A low molecular weight compound with the (1) N-H coupling indicated by JP,11-350149,A, An adhesive polymer with a C=C double bond, polybasic acid with a C=C double bond, (2) The monobasic acid in which N-H coupling consistency has an adhesive high polymer, the low-molecular-weight polybasic acid which has compatibility in it, or a C=C double bond, (3) Resin constituents, such as polybasic acid with the adhesive polymer and C=C double bond which have a C=C double bond in the resinous principle which generates N-H coupling at a hardening reaction, polybasic acid with a C=C double bond and the resinous principle which generates N-H coupling at (4) hardening reactions, and a principal chain, etc. are mentioned.

[0004] If such [to be sure] a plating inducer is used, a metal pattern (partial plating) will be easily obtained on a resin base material. However, in a actual activity, the adhesion of a metal pattern and a resin base material is important. In order to secure this adhesion, it is common physical or to roughen a resin base material front face by the chemical approach, so that surface roughness Ra may be set to several micrometers. However, the dry area of the front face by roughening is the cause which produces an electrical signal noise in the circuit board, when reducing metal pattern precision. For this reason, although the resin base material front face was roughened and it dropped off, development of the plating approach by which the high adhesion of a base material and a metal pattern is acquired was desired.

[0005]

[Problem(s) to be Solved by the Invention] this invention person paid his attention to the Plastic solid (it may only be hereafter called a Plastic solid) of the hardenability resin constituent with which it does not harden thoroughly before becoming the resin base material currently used conventionally (namely, un-hardening or semi-hardening) under this conventional technique. The initiator pattern of nonelectrolytic plating is formed in the front face of this Plastic solid, and it finds out that the high adhesion of the base material and a metal pattern concerned is acquired by using after that the resin base material which has the initiator pattern which was made to harden the Plastic solid concerned and was acquired on a front face, and came to complete this invention based on this knowledge.

[0006]

[Means for Solving the Problem] In this way, after making a plating inducer adhere to the front face of the Plastic solid of a hardenability resin constituent in the shape of [desired] a pattern according to this invention (process A), by hardening the Plastic solid of the hardenability resin constituent which passed through Process A The resin member which has the metal pattern which the resin base material which has the initiator pattern which consists of a plating inducer was obtained (process B), and the

partial plating approach which consists of what nonelectrolytic plating is performed for subsequently to the pattern top concerned (process C) was offered, and was formed by the approach concerned is offered.

[0007]

[Embodiment of the Invention] The partial galvanizing method of this invention has the following processes.

((A) Process) A plating inducer is made to adhere to the Plastic solid front face of a hardenability resin constituent in the shape of [desired] a pattern.

((B) Process) The Plastic solid which passed through Process A is hardened, and the resin base material which has the initiator pattern which consists of a plating inducer on a front face is obtained.

((C) Process) Nonelectrolytic plating on the initiator pattern on the resin base material obtained at Process B is performed.

[0008] Each process is explained below.

((A) Process) A plating inducer is made to adhere to the Plastic solid front face of a hardenability resin constituent in the shape of [desired] a pattern here. A hardenability resin constituent is a constituent containing resin, and especially if it hardens according to an operation of heat or ionizing radiation, it will not be restricted. The class of resin is not restricted according to a rank, for example, what has good moldabilities, such as an epoxy resin, maleimide resin, acrylic resin (meta), diallyl phthalate resin, triazine resin, an alicyclic olefin polymer, an aromatic series polyether polymer, a benz-cyclo-butene polymer, a cyanate ester polymer, an acenaphthylene derivative content copolymer, a liquid crystal polymer, and polyimide, is mentioned here. the inside of these -- 8-ethyl-tetracyclo [-- 4. -- the alicyclic olefin polymer (the ring-opening-polymerization object and hydrogenation object of the unsaturated hydrocarbon which has especially alicyclic structure, thing which gave these the polar group) which is a polymer which uses as a raw material the monomer which has norbornene rings, such as 4.0.12, 5.17, and a 10]-dodeca-3-en, is desirable from the point of excelling in a mechanical strength or thermal resistance.

[0009] In a hardenability resin constituent, the curing agent other than a resinous principle is usually contained. If resin is stiffened by heat or ionizing radiation, a curing agent is not restricted especially but, generally is easy to be used as a curing agent of resin. Nitrogen system curing agents, such as an isocyanurate system curing agent of halogen non-** which contains the allyl group and epoxy groups like glycidyl ether mold epoxy compound; 1-allyl compound -3, 5-diglycidyl isocyanurate, 1, and 3-diaryl-5-glycidyl isocyanurate, such as the bisphenol A screw (propylene glycol glycidyl ether) ether, as a general heat-curing agent, etc. are illustrated. As a compound stiffened by ionizing radiation, light, such as far ultraviolet rays, ultraviolet rays, and a visible ray, the bis-azide system photo-curing agent which reacts are mentioned. A flame retarder, an elasticity polymer, a heat-resistant stabilizer, a weathering stabilizer, an antioxidant, a leveling agent, an antistatic agent, a slipping agent, an anti blocking agent, an antifogger, lubricant, a color, a pigment, natural oil, synthetic oil, a wax, an emulsion, a bulking agent, an ultraviolet ray absorbent, etc. can also be added in order to raise into a constituent the component which participates in hardening, such as a hardening accelerator and a hardening assistant, and the engine performance of a resin base material.

[0010] The Plastic solid of a hardenability resin constituent is fabricated using a hardenability resin constituent which was mentioned above. As long as a Plastic solid is in the condition that the front face is not hardened thoroughly at least, it may not be hardened or may be semi-hardening. Namely, what is necessary is just the thing of a hardening condition which serves as a desired resin base material for the first time by hardening a Plastic solid further. Moreover, the part to which the plating inducer of a Plastic solid does not adhere may be hardened thoroughly. Of course, what pasted up the Plastic solid which is not hardened thoroughly on the front face of other ingredients can also be used. The Plastic solid in the condition of more specifically not hardening thoroughly is immersed in the solvent which can dissolve the hardenability resin constituent which constitutes a Plastic solid for 24 hours, the volume of

a Plastic solid swells it to 100% or more preferably 50% or more 30% or more, or a part or all dissolves it.

[0011] The configuration of a Plastic solid may not be restricted especially as long as it can form a configuration required as a resin base material behind, but what kind of configurations, such as the shape of the shape of the shape of a film and a sheet, tabular, cylindrical, and a ball, are sufficient as it. Moreover, as long as the limit exceptional in the condition on the front face of a Plastic solid has the flat part which there is not and touches a plating inducer in the touching range, it may be irregular as the whole Plastic solid front face, or may be flat.

[0012] The approach of fabricating a hardenability resin constituent is chosen as arbitration according to the configuration of a Plastic solid. For example, after mixing a hardenability resin constituent with an organic solvent, obtaining a varnish and applying this to desired thickness at a base material, the Plastic solid by which semi-hardening was carried out is acquired by carrying out clearance desiccation of the organic solvent. If needed, from a Plastic solid, a base material exfoliates and is used. Although what is necessary is just to choose the organic solvent for obtaining a varnish as arbitration according to a hardenability resin constituent, it is good for the boiling point in ordinary pressure to choose preferably 80–250 degrees C of 90–200-degree C things from a viewpoint of the balance of a moldability and productivity. What is necessary is just to perform a limit exceptional to the approach of mixing a hardenability resin constituent and an organic solvent using stirring which there is not, for example, used the magnetic stirrer with the stirring child, a high-speed homogenizer, a planet agitator, a 2 shaft agitator, a ball mill, 3 rolls, etc.

[0013] Especially the approach of applying a varnish to a base material is not restricted, for example, the approach and the solution cast method using a die coating machine, a roll coater, or a curtain coating machine, the melting cast method, etc. are mentioned in a varnish. Although especially the conditions that carry out clearance desiccation of the organic solvent are not restricted, to acquire the Plastic solid of a thermosetting resin constituent, it is necessary to adopt the conditions which are not hardened thoroughly. Although it is decided in consideration of resin, the class of curing agent, the configuration of a Plastic solid, etc. that it will be arbitration, conditions should just usually carry out desiccation clearance of the organic solvent under heating conditions of 30 seconds – 1 hour at 20–300 degrees C, when acquiring a 0.1–150-micrometer Plastic solid.

[0014] As a desirable approach of forming an initiator pattern, the method of making a plating inducer adhere to a Plastic solid front face in the shape of a direct pattern is mentioned. As the adhesion approach, the well-known adhesion approaches, such as an ink jet method which carries out fuel-spray projection of the liquid, a screen-stencil method printed through a mask, and a dispenser spreading method which applies a direct liquid, are illustrated. Adhesion actuation may be performed even once by repeating 2 times or more.

[0015] Although it is common to melt a plating inducer to water or an organic solvent, and to use by making it a solution on the occasion of adhesion, in service temperature, a plating inducer is a liquid, and especially when there is no trouble in actuation of making a plating inducer adhering with a Plastic solid front face, it is also possible not to dissolve in a solvent but to use as it is. If said Plastic solid does not dissolve the solvent which dissolves a plating inducer and a plating inducer is dissolved, there is no exceptional limit and it should just choose suitable water and the various suitable organic solvents for the approach to which a plating inducer and a Plastic solid are made to adhere. For example, in order to secure the workability of a repeat by the ink JIETO method or the screen-stencil method, it is desirable to use an volatile low polar solvent and the high (90 degrees C or more) solvent of the boiling point. Although especially the coordination structure content compound concentration in a coordination structure content compound solution is not restricted, it is usually 0.01 – 50 % of the weight preferably 0.001 to 70% of the weight from the viewpoint of the operability in this process. Moreover, to a plating inducer, in order to obtain the viscosity according to the adhesion approach, thickeners, such as Aerosil, etc. may be added in order to give thixotropy nature. Although the temperature for adhesion can be

chosen as arbitration in consideration of the boiling point of a plating inducer or its solution, the melting point, operability, productivity, etc., it is usually preferably performed at 15–65 degrees C 10–100 degrees C. After making a plating inducer adhere to a Plastic solid front face, after treatment of blowing inert gas, such as nitrogen, drying 30–180 degrees C in 5 – 120 minutes and in oven preferably 1 minute or more at 50–150 degrees C which rinses a Plastic solid front face may be carried out in order to remove a superfluous plating inducer.

[0016] If a plating inducer has the property to be easy for plating and a plating catalyst to adsorb, a well-known thing which an exceptional limit does not have and was indicated by the official report mentioned above can be used for it. In order to acquire the more excellent adhesion, it is desirable to use the compound which has metal coordination ability. The thing desirable as a compound (it may be hereafter called a coordination structure content compound) which has metal coordination ability has the compound which has unshared electron pairs, such as a heterocyclic compound which has coordination ability with the compound metallurgy group which has the functional group which can be configured to metals, such as an amino group, a thiol group, a carboxyl group, and a cyano group. Especially the heterocyclic compound that contains a nitrogen atom, an oxygen atom, or a sulfur atom especially is desirable, and the heterocyclic compound which especially contains a nitrogen atom is desirable. Of course, such a heterocyclic compound may also have the functional group which can further be configured to a metal. Furthermore, the heterocyclic compound which also has the functional group which can be configured to a metal is desirable at the point of giving higher pattern adhesion.

[0017] From the point firmly held on the resin base material front face in which it reacts to with the component in a hardenability resin constituent, and these compounds are formed at the following process also in a coordination structure content compound An imidazole, 2-methylimidazole, 2-ethyl-4-methylimidazole, A 2-mercaptomethyl benzimidazole and 2-ethyl imidazole-4-dithiocarboxylic acid, A 2-methylimidazole-4-carboxylic acid, 1 -(2-aminoethyl)- 2-methylimidazole, 1 -(2-cyano ethyl)- 2-methylimidazole, 2-phenyl-4, 5-dihydroxymethylimidazole, Imidazole derivatives, such as benzimidazole and a 2-ethyl-4-thio carbamoyl imidazole; A pyrazole, Pyrazoles, such as a 3-amino-4-cyano-pyrazole; 1, 2, 4-triazole, 2-amino - 1, 2, 4-triazole, 1, 2-diamino - 1, 2, 4-triazole, 1-mercapto - Triazole; 2-amino triazine, such as 1, 2, and 4-triazole, 2, 4-diamino - 6 - (triazine;., such as 6-(2-(2 methyl-1-imidazolyl) ethyl) triazine 2 and 4 and 6-trimercapto-s-triazine-TORISODEIUMU salt, is raised as a desirable example.)

[0018] ((B) Process) Here, the Plastic solid which passed through Process A is hardened, and the resin base material which has an initiator pattern on a front face is obtained. What is necessary is just to choose the approach of hardening according to the property of a Plastic solid. For example, what is necessary is for what is necessary to be just to harden a Plastic solid by Lycium chinense on heating conditions, if it is the Plastic solid of a thermosetting resin constituent, and just to harden by irradiating light, an electron ray, etc. like far ultraviolet rays, ultraviolet rays, and a visible ray, if it is the Plastic solid of an ionizing-radiation hardenability resin constituent. For example, when hardening the Plastic solid of a thermosetting resin constituent, 70–300 degrees C of temperature for making it harden are 30–400 degrees C usually 100–200 degrees C more preferably, and the setting time is usually 0.5 – 3 hours preferably for 0.1 to 5 hours. What is necessary is not to restrict especially the approach of heating, for example, just to perform it using oven etc.

[0019] A Plastic solid is thoroughly hardened by hardening and serves as a resin base material which has an initiator pattern on a front face by it. Conventionally, it is the point in which the initiator pattern was formed on the resin base material which comes to harden a Plastic solid thoroughly, and differs from this invention greatly. After forming an initiator pattern in the Plastic solid front face which is not hardened thoroughly, adhesion with the plating which is hardening a Plastic solid, and is formed in a resin base material front face on it since a plating inducer is incorporated and a plating inducer and a resin base material are combined firmly also increases. After roughening a resin base material front face, it is

not necessary to form an initiator pattern, and according to the approach of this invention, the flat resin base material of an interface with the initiator pattern (metal pattern) of a resin base material is obtained. Flatness means that 200nm or less of 100nm or less of surface roughness Ra is 80nm or less more preferably here. In addition, surface roughness Ra is JIS here. B It is the value computed based on a convention of 0601.

[0020] When the coordination structure content compound mentioned above is used, the crosslinking density on the front face of a Plastic solid can be raised more at the time of hardening in Process B. For this reason, the dry area of the resin base material produced in a resin base material front face or an interface with the initiator pattern of a resin base material can be stopped at the oxidation process of the resin base material front face performed if needed [of next explaining in full detail].

[0021] By hardening in this process B, a layer weak against a resin base material front face may be formed, or a pollutant may adhere from a hardening ambient atmosphere. Then, it is desirable to oxidize a base material front face (process B') in order to remove these. Although there is no exceptional limit in the approach of oxidizing a base material front face, since a base material front face is not damaged, the method of contacting a chemical on base material front faces, such as an approach using the solution of an oxidizing quality compound and an approach using a gas medium, is desirable.

[0022] As an oxidizing quality compound, well-known oxidizing quality compounds which have oxidation ability, such as an inorganic peroxide and organic peroxide, can be used. As an inorganic peroxide, a permanganate, a chromic anhydride, dichromate, a chromate, persulfate, an activity manganese dioxide, an osmium tetroxide, a hydrogen peroxide, fault iodine acid chloride, ozone, etc. are mentioned, and dicumyl peroxide, octanoyl peroxide, m-chloro perbenzoic acid, a peracetic acid, etc. are mentioned as organic peroxide. There is no limit exceptional to the approach of oxidizing a resin base material front face using an oxidizing quality compound, for example, after dissolving in the medium which can dissolve these if needed and making an oxidizing quality compound liquefied, general approaches, such as an approach of making the resin base material after hardening contacting, are mentioned. As a medium used for dissolving an oxidizing quality compound, polar organic solvents, such as neutral organic solvents, such as aqueous acids, such as alkali water solutions, such as neutral water and a NaOH water solution, and a sulfuric-acid water solution, the ether, and the petroleum ether, an acetone, and a methanol, are illustrated. Limits exceptional to the approach of contacting an oxidizing quality compound on a resin base material front face may be what kind of approaches, such as a dip method which there is not, for example, is immersed in an oxidizing quality compound solution in a resin base material, the liquid peak method for putting an oxidizing quality compound solution on the front face of a base material using surface tension, and a spray method which sprays an oxidizing quality compound solution on a base material. That what is necessary is just to set as arbitration the temperature and time amount which contact these oxidizing quality compounds on a resin base material front face in consideration of the concentration of a peroxide, a class, the contact approach, etc., 10-250 degrees C of temperature are usually 20-180 degrees C preferably, and time amount is 1 minute - 30 minutes preferably for 0.5 to 60 minutes. Under the minimum of clearance of this range may be inadequate in the pollutant which adhered from the weak layer and hardening ambient atmosphere of the resin base material front face produced by hardening after hardening, or if the upper limit of this range is exceeded, a resin base material front face may become weak, or surface smooth nature may be spoiled.

[0023] After contacting an oxidizing quality compound on a resin base material front face, in order to remove an oxidizing quality compound, a resin base material is usually washed with water. When the matter which cannot be washed only with water adheres to a base material, after washing further by the penetrant remover which can dissolve the matter, or making other compounds contact and making it the matter meltable in water, it can also wash with water. For example, when alkaline water solutions, such as a potassium permanganate water solution and a sodium permanganate water solution, are contacted to a resin base material, it is the object which removes the coat of the generated manganese dioxide, and neutralization reduction processing is carried out by aqueous acids, such as mixed liquor of a

sulfuric-acid hydroxy amine and a sulfuric acid.

[0024] As an approach of oxidizing using a gas medium, radical-izing and well-known plasma treatment with possible making it ionize are mentioned in media, such as reverse sputtering and corona discharge. As a gas medium, atmospheric air, oxygen, nitrogen, an argon, water, a carbon disulfide, a carbon tetrachloride, etc. are illustrated. When a medium is liquefied in a processing temperature ambient atmosphere, after evaporating under reduced pressure, oxidation treatment is carried out, and in a processing temperature ambient atmosphere, in the case of a gas, a medium carries out oxidation treatment, after pressurizing the pressure in which radical-izing and ionization are possible. That what is necessary is just to set as arbitration the temperature and time amount which contact the plasma on a resin base material front face in consideration of a class, a flow rate, etc. of gas, 10–250 degrees C of temperature are usually 20–180 degrees C preferably, and time amount is usually 1 minute – 30 minutes preferably for 0.5 to 60 minutes.

[0025] ((C) Process) Here, nonelectrolytic plating is performed on the initiator pattern on the resin base material pass Process B. Usually, processings, such as grant of a plating catalyst and activation of a catalyst, are performed before nonelectrolytic plating. Plating catalysts are the metallic compounds used as a reduction catalyst with the operation to which a deposit of plating is carried out in nonelectrolytic plating liquid. As a metal, Pd, Pt, Au, Ag, Ir, Os, Ru, Sn, Zn, Co, etc. are mentioned. In order to raise adhesion, Pd amine complex, sulfuric-acid palladium, a palladium chloride, etc. are preferably [using a metaled generable organometallic complex and a metaled metal salt by reduction] as metallic compounds, and specifically mentioned. After being immersed in the liquid (an acid, alkali, the complexing agent, the reducing agent, etc. may be contained if needed) which dissolved metallic compounds in organic solvents, such as water, alcohol, or chloroform, by 0.001 – 10% of the weight of concentration as the approach of activation of catalyst grant and a catalyst and giving a plating catalyst, the approach of returning a metal and activating a catalyst etc. is mentioned. Although many catalysts adsorb according to an initiator pattern, it is desirable to remove the catalyst which stuck to the part without an initiator pattern. Usually, when clearance rinses an unnecessary catalyst after catalyst grant and activation of a catalyst, it carries out.

[0026] Thus, give the catalyst activated on the initiator pattern of a resin base material, subsequently nonelectrolytic plating liquid is made to contact, and nonelectrolytic plating is performed. Although there is no exceptional limit in the nonelectrolytic plating liquid used for nonelectrolytic plating, the nonelectrolytic plating liquid of a desirable well-known autocatalysis mold is used. As an example of nonelectrolytic plating liquid, hypophosphorous acid ammonium or hypophosphorous acid, The non-electrolytic copper plating liquid which uses potassium-borohydride ammonium, a hydrazine, formalin, etc. as a reducing agent, The non-electrolyzed nickel-Lynn plating liquid which uses sodium hypophosphite as a reducing agent, The non-electrolyzed nickel-boron plating liquid which uses dimethylamine borane as a reducing agent, Nonelectrolytic plating liquid, such as non-electrolyzed palladium plating liquid, non-electrolyzed palladium-Lynn plating liquid which uses sodium hypophosphite as a reducing agent, non-electrolyzed gilding liquid, non-electrolyzed silver plating liquid, and non-electrolyzed nickel-cobalt-Lynn plating liquid that uses sodium hypophosphite as a reducing agent, can be used. After nonelectrolytic plating, a substrate front face can be contacted to a rust-proofer, and rustproofing can also be carried out.

[0027] After performing nonelectrolytic plating and making a metal pattern form in a resin base material front face, in order to raise adhesion, it is desirable to be 80–250 degrees C preferably, and to heat-treat preferably 50–350 degrees C of resin base materials for 0.1 to 5 hours for 0.1 to 10 hours using oven etc., (process D). At this time, it is desirable to heat under inert gas ambient atmospheres, such as nitrogen and an argon. Furthermore, a resin base material may be pressurized with a press plate etc. if needed at the time of heating.

[0028] The resin member of this invention which has a metal pattern on a front face is obtained by performing nonelectrolytic plating to a resin base material front face through the above processes. This

resin member can be used as a printed-circuit board used for for example, semiconductor device mounting components, various panel indicating equipments, an IC card, and an optical device.

[0029]

[Example] An example and the example of a comparison are given to below, and this invention is concretely explained to it. In addition, among an example, the section and % are weight criteria, as long as there is no notice especially. The assessment approach performed in this example is as follows.

(1) Molecular weight (Mw, Mn)

It measured as a polystyrene reduced property by the gel permeation chromatography (GPC) which uses toluene as a solvent.

(2) the mol of the unsaturated bond in the polymer before the rate of hydrogenation, and (anhydrous) maleic-acid residue content hydrogenation -- the mol of the maleic-acid residue to the rate of hydrogenation to a number (hydrogenation appending rate), and the total number of monomeric units in a polymer (anhydrous) -- a number -- it measured with ¹H-NMR spectrum comparatively (carboxyl group content).

(3) Glass transfer temperature (Tg)

It measured by the differential scan heating-value method (DSC law).

(4) The granularity atomic force microscope on the front face of resin (the product made from Digital Instrument , Nanoscope 3a) measured and estimated surface average-of-roughness-height Ra in the tapping mode in atmospheric air using Si single crystal stick-shape cantilever (load rate = 20 N/m, die length of 125 micrometers). Ra is JIS. B It is the arithmetic mean granularity set to 0601.

(5) Assessment JIS of adhesion C 5012 JIS after leaving the multilayer substrate in which the assessment pattern of the plating adhesion set to 8.5 was formed to the outermost layer of drum for 24 hours, in the ambient atmosphere of 65% of temperature relative humidity of 25 degrees C C 5012 Plating adhesion was examined according to 8.5 and exfoliation of a plating layer and generating of a float were observed visually. That by which good, and exfoliation and a float are observed in that by which neither exfoliation nor a float is observed was made into the defect.

(6) 50 circuit patterns were formed by assessment wiring width of face of 30 micrometers of patterning nature, the distance between wiring of 30 micrometers, and 5cm of wire lengths, and although turbulence was in O and a configuration about some where each of 50 do not have turbulence in a configuration, what has ** and a deficit in a thing without a deficit was evaluated as x.

[0030] example 18-ethyl-tetracyclo [-- 4. -- 4.0.12, 5.17, and a 10]-dodeca-3-en -- ring opening polymerization -- carrying out -- subsequently -- a hydrogenation reaction -- carrying out -- (number-average-molecular-weight Mn) =31,200, weight-average-molecular-weight (Mw) =55,800, and Tg= -- about 140-degree C hydrogenation polymer was obtained. The rate of hydrogenation of the obtained polymer was 99% or more. The polymer 100 section, the maleic-anhydride 40 section, and the JIKUMIRU peroxide 5 section which were obtained were dissolved in the t-butylbenzene 250 section, and the reaction was performed at 140 degrees C for 6 hours. Poured out the obtained resultant solution into the isopropyl alcohol of the 1000 sections, the resultant was made to solidify, and the maleic-acid denaturation hydrogenation polymer was obtained. The vacuum drying of this denaturation hydrogenation polymer was carried out at 100 degrees C for 20 hours. Tg of the molecular weight of this denaturation hydrogenation polymer was 170 degrees C in Mn=33,200 and Mw=68,300. (Anhydrous) Maleic-acid residue content was 25-mol %.

[0031] Said denaturation hydrogenation polymer 100 section, the bisphenol A screw (propylene glycol glycidyl ether) ether 40 section, the 2-[2-hydroxy-3 and 5-screw (alpha and alpha-dimethylbenzyl) phenyl] benzotriazol 5 section, and the 1-benzyl-2-phenylimidazole 0.1 section were dissolved in the partially aromatic solvent which consists of the xylene 215 section and the cyclopentanone 54 section, and the varnish of a hardenability resin constituent was obtained.

[0032] Using the die coating machine, coating of the varnish concerned was carried out to the polyethylenenaphthalate film (carrier film) with a thickness [of 300mm angle] of 40 micrometers, it was

dried for 10 minutes at 120 degrees C among nitrogen oven after that, and the dry-with carrier film film whose thickness of a resin (equivalent to Plastic solid of hardenability resin constituent) layer is 35 micrometers was obtained.

[0033] On the other hand, 0.1% isopropyl alcohol solution of 2-G n-butylamino -4 and 6-dimercapto-s-triazine is prepared. Wiring width of face and the distance between wiring in this solution 50 micrometers, Conductor thickness is immersed for 1 minute at 25 degrees C in the double-sided copper-clad substrate (core material which was made to carry out impregnation of the varnish containing a glass filler and a halogen non-** epoxy resin to glass fabrics, and was obtained) with a thickness of 0.8mm with which the front face had the inner layer circuit by which micro etching processing was carried out formed by 18 micrometers. Subsequently, made it dry in the oven by which the nitrogen purge was carried out for 15 minutes at 90 degrees C, the primer layer was made to form, and the inner layer substrate was obtained.

[0034] On the above-mentioned inner layer substrate, the above-mentioned dry-with carrier film film was piled up to double-sided copper-clad substrate both sides, as the resin side became the inside. This was decompressed to 200Pa using the vacuum laminator equipped with the press plate made of heat-resistant rubber up and down as a primary press, and heating sticking by pressure was carried out for 60 seconds by the temperature of 110 degrees C, and pressure 0.5MPa. Subsequently, using the vacuum laminator equipped with the press plate made of heat-resistant rubber covered with the metal press plate as a secondary press up and down, it decompresses to 200Pa, and for 60 seconds, heating sticking by pressure was carried out and the laminating of the Plastic solid of a hardenability resin constituent was carried out by the temperature of 140 degrees C, and 1.0MPa.

[0035] Only the polyethylenenaphthalate film was removed from the substrate to which the laminating of the Plastic solid of the above-mentioned hardenability resin constituent was carried out. Ra was 14nm when the surface roughness of the Plastic solid of a hardenability resin constituent was evaluated. Subsequently, to the Plastic solid front face of the hardenability resin constituent by which the laminating was carried out to this substrate, it is 1 as a plating inducer. -(2-aminoethyl)- The water solution prepared so that 2-methylimidazole might become 0.3% was drawn to the desired circuit pattern using ink jet equipment, and the initiator pattern for nonelectrolytic plating was formed in the Plastic solid front face. This was left for 60 minutes in 170-degree C nitrogen oven, the Plastic solid of a hardenability resin constituent was stiffened, the electric insulation layer which is a resin base material was formed on the inner layer substrate, and the laminate was obtained. In addition, the initiator pattern is formed in the front face of this laminate. The 3rd higher harmonic wave of UV-YAG laser was used for a part for the insulating layer of the obtained laminate, the beer hall of an interlayer connection with a diameter of 30 micrometers was formed, and the multilayer substrate with a beer hall was obtained.

[0036] Splash immersion was carried out for 10 minutes at the 80-degree C water solution which adjusted the above-mentioned multilayer substrate with a beer hall as plating pretreatment so that it might become the permanganic acid concentration of 60g/l., and the sodium-hydroxide concentration of 28g/l., and the front face was oxidized. Subsequently, the substrate was rinsed by carrying out splash immersion of the substrate for 1 minute at a cistern, and carrying out splash immersion for 1 minute at still more nearly another cistern. Then, after immersing the substrate in the 25-degree C water solution adjusted so that it might become the hydroxylamine sulfate concentration of 170g/l., and a 80g [/l.] sulfuric acid for 5 minutes and carrying out neutralization reduction processing to it, rinsing was carried out, nitrogen was sprayed and water was removed.

[0037] It was immersed in 60-degree C Pd salt content plating catalyst solution with which activator MAT-1-A (the Kamimura Industries make) adjusted the multilayer substrate after rinsing so that 200ml [// l.] and activator MAT-1-B (the Kamimura Industries make) might become in 30ml [l.] /and a sodium hydroxide might become in 1g/l. for 5 minutes for plating catalyst grant. Subsequently, after rinsing a substrate by the same approach as **** for catalytic-activity-izing, 18ml [// l.] and reducer MRD-2-C (the Kamimura Industries make) was immersed in the solution adjusted so that it might

become [I.] in 60ml /for 5 minutes at 35 degrees C, and reducer MRD-2-A (the Kamimura Industries make) carried out reduction processing of the plating catalyst. Thus, when the granularity of the outermost insulating-layer front face of the multilayer substrate which the plating catalyst was made to adsorb and was obtained was evaluated, Ra of the part into which Ra of the part which drew the pattern has not drawn 32nm and a pattern was the almost same Ra value as 29nm.

[0038] SURUKAPPU PRX-1-A (the Kamimura Industries make) the obtained multilayer substrate In this way, 150ml/l. SURUKAPPU PRX-1-B (the Kamimura Industries make) blowing air into the 25-degree C nonelectrolytic plating liquid adjusted so that 100ml [// I.] and SURUKAPPU PRX-1-C (the Kamimura Industries make) might become [I.] in 20ml / It was immersed for 15 minutes, nonelectrolytic plating processing was carried out, it rinsed like ****, and the multilayer substrate with which the metal pattern was formed in the shape of [desired] a pattern was obtained. SURUKAPPU ELC-SP-A (the Kamimura Industries make) in order to increase the thickness of a metal pattern Subsequently, 80ml/l.

SURUKAPPU ELC-SP-B (the Kamimura Industries make) 20ml/l. SURUKAPPU ELC-SP-C (the Kamimura Industries make) 80ml/l. The metal was further piled up in the shape of [which was immersed for 5 hours and formed in the point with a nonelectrolytic plating processing almsgiving thickness of 18 micrometers] a metal pattern, blowing air into the 60-degree C high-speed nonelectrolytic plating liquid adjusted so that SURUKAPPU ELC-SP-D (the Kamimura Industries make) might become [I.] in 20ml /. Furthermore, it rinsed like **** and the multilayer substrate with which the metal pattern was formed in the shape of [desired] a pattern was obtained. Subsequently, it dried to the inhibited de-rusting solution adjusted so that AT-21 (the Kamimura Industries make) might become [I.] in 10ml /, and 25 degrees C of rustproofing were performed to it, after being immersed for 1 minute and rinsing by the still more nearly same approach as ****.

[0039] The multilayered circuit board which has the metal pattern which left the multilayer substrate with which this rustproofing was performed for 30 minutes, heat-treated it at 170 degrees C in the oven of nitrogen-gas-atmosphere mind, and was formed by said non-electrolytic copper plating to both sides was obtained. Ra was 31nm when the granularity of the electric insulation layer (resin base material) front face of a part without the pattern of the obtained multilayered circuit board was evaluated. Assessment of the patterning nature of the obtained multilayered circuit board and assessment of plating adhesion were performed. An assessment result is shown in a table 1.

[0040] Example 21 -(2-aminoethyl)- AEROJILRY200 [15-section] (product made from Japanese Aerosil, Inc.) was added in order to give thixotropy nature to the water-solution 100 section adjusted so that 2-methylimidazole might become 0.3%, and the distributed solution which carried out mixed distribution with the peripheral speed of 10m/second using the dissolver was adjusted. 1 of an example 1 -(2-aminoethyl)- It replaced with the water solution adjusted so that 2-methylimidazole might become 0.3%, and carried out like the example 1 except having changed into screen-stencil equipment the equipment used in order to draw to an initiator pattern using this distributed solution. When the granularity of the outermost insulating-layer front face after carrying out plating pretreatment was evaluated, Ra of the part which is not printing 58nm of Ra of the part which printed the initiator pattern was the almost same Ra value as 32nm. Ra was 33nm when the granularity on the front face of an insulating layer of a part without the pattern of the obtained multilayered circuit board was evaluated. The assessment result of the pattern adhesion of the obtained multilayered circuit board and patterning nature is shown in a table 1.

[0041] except not carrying out permanganic acid processing in the example of comparison 1 example 1, it was alike like the example 1, it carried out, and the multilayered circuit board was obtained. When the granularity of the outermost insulating-layer front face after carrying out plating pretreatment was evaluated, Ra of the part into which Ra of the part which has drawn the pattern has not drawn 31nm and a pattern was 26nm. Ra was 31nm when the granularity on the front face of an insulating layer of a part without the pattern of the obtained multilayered circuit board was evaluated. The assessment result of the pattern adhesion of the obtained multilayered circuit board and patterning nature is shown in a

table 1.

[0042]

[A table 1]

(表 1)

実施例	密着性	パターンニング性
実施例 1	良	○
実施例 2	良	○
比較例 1	不良	△

[0043] When the initiator pattern which consists of a plating inducer was formed in the hardenability resin Plastic solid front face before hardening from the above result, it turned out that the adhesion which was excellent in the resin base material front face after hardening compared with the case where an initiator pattern is formed is acquired. Especially the partial galvanizing method of this invention does not need to roughen a resin base material front face, and the small resin member of the surface roughness of the resin base material in an interface with a metal pattern is obtained. For this reason, it is suitable also for manufacture of the circuit board the problem of using the roughened resin base material is indicated to be.

[Translation done.]

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(54) 【発明の名称】 部分めっき方法及び樹脂部材

(57) 【要約】

【課題】 粗化処理を必要としない、パターン密着性に優れた部分めっき法を提供する。

【解決手段】 硬化性樹脂組成物の成形体の表面に、所望のパターン状にめっき誘発物質を付着させた（工程A）後、工程Aを経た硬化性樹脂組成物の成形体を硬化することにより、めっき誘発物質からなるイニシエータパターンを有する樹脂基材を得（工程B）、次いで当該パターン上に無電解めっきを行う（工程C）部分めっき法。

(2)

【特許請求の範囲】

【請求項1】 硬化性樹脂組成物の成形体の表面に、所望のパターン状にめっき誘発物質を付着させた（工程A）後、工程Aを経た硬化性樹脂組成物の成形体を硬化することにより、めっき誘発物質からなるイニシエータパターンを有する樹脂基材を得（工程B）、次いで当該パターン上に無電解めっきを行う（工程C）ことから成る部分めっき方法。

【請求項2】 めっき誘発物質が金属配位能を有する化合物からなるものである請求項1記載の部分めっき方法。

【請求項3】 工程Bにおける硬化が熱により行われるものである請求項1記載の部分めっき方法。

【請求項4】 工程Cの前に、樹脂基材表面を酸化する（工程B'）請求項1記載の部分めっき方法。

【請求項5】 工程Cの後、樹脂基材を加熱する工程（工程D）を有する請求項1記載の部分めっき方法。

【請求項6】 請求項1～5のいずれかの方法により形成された金属パターンを有する樹脂部材。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、樹脂基材表面に金属パターンを形成するための部分めっき方法に関する。

【0002】

【従来の技術】半導体デバイス、半導体デバイス実装部品、各種パネル表示装置、ICカード、光デバイス等には、樹脂基材（以下、単に基材ということがある）表面に金属微細線（金属パターン）を有する樹脂部材が用いられている。こうした金属微細線（金属パターン）の形成は、めっきによって行われるのが一般的である。めっきによる金属パターン形成方法は、大別して、樹脂基材の全面に無電解めっきを施した後、マスクパターンを介して電解めっきにより金属を成長させ、次いで不要な無電解めっきを除去する方法と、樹脂基材に無電解めっきを所望のパターン状にめっき（部分めっき）して直接金属パターンを形成し、必要に応じてその上にめっきを成長させる方法とに分けられる。部分めっきを利用した後者の方法は、不要な無電解めっきを除去する際に用いる薬品等による金属腐食が生じない上、無電解めっき除去工程が不要であることから、生産性に優れる。

【0003】部分めっきに際して、めっき誘発物質からなるイニシエータパターン（無電解めっき用被膜ともいう）を樹脂基材表面に形成し、このパターン上にめっきをすると、容易に金属パターンが得られることが知られている（特開平7-263841号公報など）。めっき誘発物質については、樹脂基材への付着性やパターン形状の改良を目的として多くの検討がなされている。めっき誘発物質の例としては、導電性高分子又はその前駆体と水又は極性溶剤との混合物からなる導電性材料（特開2002-26014号公報）、可溶性パラジウム塩

2

と水溶性の溶剤と水とからなる組成物（特開平7-131135号公報、特開平7-245467号公報）、感光性パラジウム高分子キレート化合物を含有する材料

（特開2000-147762号公報）、特開平11-350149号公報に開示された（1）N-H結合を持つ低分子量化合物、C=C二重結合を持つ接着性ポリマー、C=C二重結合を持つ多塩基酸、（2）N-H結合密度が高い接着性ポリマー、それに相溶性のある低分子量多塩基酸又はC=C二重結合を持つ一塩基酸、（3）硬化反応でN-H結合を生成する樹脂成分とC=C二重結合を持つ多塩基酸、（4）硬化反応でN-H結合を生成する樹脂成分と主鎖にC=C二重結合を持つ接着性ポリマー及びC=C二重結合を持つ多塩基酸などの樹脂組成物等が挙げられる。

【0004】確かにこのようなめっき誘発物質を用いれば、容易に樹脂基材上に金属パターン（部分めっき）が得られる。しかし、実際の使用においては、金属パターンと樹脂基材との密着性が重要となっている。この密着性を確保するため、樹脂基材表面を物理的或いは化学的方法により、表面粗さRaが数 μm になるように粗化するのが一般的である。しかしながら、粗化による表面の荒れは、金属パターン精度を低下させる上、回路基板では電気信号ノイズを生じる原因となっている。このため、樹脂基材表面を粗化しなくても基材と金属パターンとの高い密着性が得られるめっき方法の開発が望まれていた。

【0005】

【発明が解決しようとする課題】かかる従来技術の下、本発明者は、従来使用されていた樹脂基材となる前の、完全には硬化されていない（即ち、未硬化又は半硬化の）硬化性樹脂組成物の成形体（以下、単に成形体と言うことがある）に着目した。この成形体の表面に無電解めっきのイニシエータパターンを形成し、その後、当該成形体を硬化させて得られたイニシエータパターンを表面に有する樹脂基材を用いることで、当該基材と金属パターンとの高い密着性が得られることを見だし、この知見に基づいて本発明を完成するに至った。

【0006】

【課題を解決するための手段】かくして、本発明によれば、硬化性樹脂組成物の成形体の表面に、所望のパターン状にめっき誘発物質を付着させた（工程A）後、工程Aを経た硬化性樹脂組成物の成形体を硬化することにより、めっき誘発物質からなるイニシエータパターンを有する樹脂基材を得（工程B）、次いで当該パターン上に無電解めっきを行う（工程C）ことから成る部分めっき方法が提供され、また当該方法により形成された金属パターンを有する樹脂部材が提供される。

【0007】

【発明の実施の形態】本発明の部分めっき法は、以下の工程を有する。

(3)

3

(工程A) 硬化性樹脂組成物の成形体表面に、所望のパターン状にめっき誘発物質を付着させる。

(工程B) 工程Aを経た成形体を硬化して、めっき誘発物質からなるイニシエータパターンを表面に有する樹脂基材を得る。

(工程C) 工程Bで得られた樹脂基材上にあるイニシエータパターン上の無電解めっきを行う。

【0008】以下に各工程を説明する。

(工程A) ここでは、硬化性樹脂組成物の成形体表面に、所望のパターン状にめっき誘発物質を付着させる。硬化性樹脂組成物は、樹脂を含有する組成物であって、熱や電離放射線の作用により硬化するものであれば特に制限されない。ここで樹脂の種類は格別に制限されず、例えば、エポキシ樹脂、マレイミド樹脂、(メタ)アクリル樹脂、ジアリルフタレート樹脂、トリアジン樹脂、脂環式オレフィン重合体、芳香族ポリエーテル重合体、ベンゾシクロブテン重合体、シアネートエステル重合体、アセナフチレン誘導体含有共重合体、液晶ポリマー、ポリイミドなど成形性の良いものが挙げられる。これらの中でも、8-エチルテトラシクロ[4.4.0.1².5.1⁷.1⁰]ノルボルネン環を有する単量体を原料とする重合体である脂環式オレフィン重合体(特に脂環式構造を有する不飽和炭化水素の開環重合体とその水素添加物、又はこれらに極性基を付与したもの)は、機械的強度や耐熱性に優れる点から好ましい。

【0009】硬化性樹脂組成物中には、通常、樹脂成分の他に、硬化剤を含有する。硬化剤は、熱又は電離放射線により樹脂を硬化させるものであれば、特に制限されず、一般的に樹脂の硬化剤として用いられているもので良い。一般的な熱硬化剤としては、ビスフェノールAビス(プロピレングリコールグリシジルエーテル)エーテルなどのようなグリシジルエーテル型エポキシ化合物；1-アリル-3,5-ジグリシジルイソシアヌレート、1,3-ジアリル-5-グリシジルイソシアヌレートのごときアリル基とエポキシ基とを含有するハロゲン不含のイソシアヌレート系硬化剤などの窒素系硬化剤等が例示される。電離放射線により硬化させる化合物としては、遠紫外線、紫外線、可視光線などの光と反応するビスアジド系光硬化剤などが挙げられる。組成物中には、硬化促進剤や硬化助剤など硬化に関与する成分や、樹脂基材の性能を高める目的で、難燃剤、軟質重合体、耐熱安定剤、耐候安定剤、老化防止剤、レベリング剤、帯電防止剤、スリップ剤、アンチブロッキング剤、防曇剤、滑剤、染料、顔料、天然油、合成油、ワックス、乳剤、充填剤、紫外線吸収剤などを添加することもできる。

【0010】硬化性樹脂組成物の成形体は、上述したような硬化性樹脂組成物を用いて成形されたものである。成形体は、少なくとも表面が完全には硬化されていない状態であれば、未硬化であっても半硬化であってもよ

4

い。即ち、成形体を、さらに硬化することによって、初めて所望の樹脂基材となるような硬化状態のものであれば良い。また、成形体の、めっき誘発物質が付着しない部分は完全に硬化されていてもよい。もちろん、完全には硬化されていない成形体を、他の材料の表面に接着したものをを用いることもできる。より具体的には、完全には硬化されていない状態にある成形体は、成形体を構成する硬化性樹脂組成物を溶解可能な溶剤に24時間浸漬することで、成形体の体積が、30%以上、好ましくは50%以上、より好ましくは100%以上に膨潤するか、一部もしくは全てが溶解するものである。

【0011】成形体の形状は、後に樹脂基材として必要な形状を形成しうるものであれば特に制限されず、フィルム状、シート状、板状、円筒状、球状などいかなる形状でも良い。また成形体表面の状態に格別な制限はなく、めっき誘発物質と接する部分が、その接する範囲で平坦であれば、成形体表面全体として凹凸があっても、平坦であってもよい。

【0012】硬化性樹脂組成物を成形する方法は、成形体の形状に応じて任意に選択される。例えば、硬化性樹脂組成物を有機溶剤と混合してワニスを得、これを支持体に、所望の厚みに塗布した後、有機溶剤を除去乾燥することで、半硬化された成形体を得られる。支持体は必要に応じて、成形体から剥離して用いる。ワニスを得るための有機溶剤は、硬化性樹脂組成物に応じて任意に選択すればよいが、成形性と生産性のバランスの観点から、常圧での沸点が80~250℃、好ましくは90~200℃のものを選択するのがよい。硬化性樹脂組成物と有機溶剤とを混合する方法に格別な制限はなく、例えば、攪拌子とマグネチックスターラーを使用した攪拌、高速ホモジナイザー、遊星攪拌機、二軸攪拌機、ボールミル、三本ロールなどを使用して行えばよい。

【0013】ワニスを支持体に塗布する方法は、特に制限されず、例えば、ワニスをダイコーター、ロールコーター又はカーテンコーターによりを用いた方法や溶液キャスト法や溶融キャスト法などが挙げられる。有機溶剤を除去乾燥する条件は特に制限されないが、熱硬化性の樹脂組成物の成形体を得る場合は、完全には硬化しない条件を採用する必要がある。条件は、樹脂や硬化剤の種類や成形体の形状などを考慮し、任意に決定されるが、0.1~150μmの成形体を得る場合、通常20~300℃で30秒~1時間の加熱条件下で、有機溶剤を乾燥除去すればよい。

【0014】イニシエータパターンを形成する好ましい方法として、めっき誘発物質を、成形体表面に直接パターン状に付着させる方法が挙げられる。付着方法としては、液体を噴霧突出させるインクジェット方式、マスクを介して印刷するスクリーン印刷方式、直接液体を塗布するディスペンサ塗布方式など、公知の付着方法が例示される。付着操作は、1回でも2回以上を繰り返して行っ

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てもよい。

【0015】付着に際しては、めっき誘発物質を水又は有機溶媒に溶かして溶液にして用いるのが一般的であるが、使用温度においてめっき誘発物質が液体であり、めっき誘発物質を成形体表面と付着させる操作に支障がない場合は、特に溶媒に溶解せず、そのまま用いることも可能である。めっき誘発物質を溶解する溶媒は、前記成形体が溶解しないものであり、かつめっき誘発物質を溶解するものであれば格別な制限はなく、めっき誘発物質と成形体とを付着させる方法に適切な、水や各種有機溶剤を選択すれば良い。例えば、インクジェット方式やスクリーン印刷方式では、繰り返しの作業性を確保するために、揮発性の低い極性溶媒や沸点の高い（90℃以上）溶媒を用いるのが好ましい。配位構造含有化合物溶液中の配位構造含有化合物濃度は特に制限されないが、本工程での操作性の観点から、通常0.001～70重量％、好ましくは0.01～50重量％である。また、付着方法に応じた粘度を得るため、めっき誘発物質には、チキソトロピー性を付与する目的でアエロジルなどの増粘剤等を添加しても良い。付着に際しての温度は、めっき誘発物質やその溶液の沸点、融点、操作性や生産性などを考慮して任意に選択することができるが、通常10～100℃、好ましくは15～65℃で行う。めっき誘発物質を成形体表面に付着させた後、過剰なめっき誘発物質を除去する目的で、成形体表面を水洗する、窒素などの不活性ガスを吹きかける、30～180℃、好ましくは50～150℃で1分以上、好ましくは5～120分間、オープン中で乾燥させるなどの後処理をしてもよい。

【0016】めっき誘発物質は、めっきやめっき触媒が吸着されやすい性質を有するものであれば格別な制限はなく、前述した公報に記載されたような公知のものを用いることができる。より優れた密着性を得るためには、金属配位能を有する化合物を用いるのが好ましい。金属配位能を有する化合物（以下、配位構造含有化合物ということがある）として好ましいのは、アミノ基、チオール基、カルボキシル基、シアノ基など金属に配位可能な官能基を有する化合物や金属との配位能を有する複素環化合物などの非共有電子対を有する化合物がある。中でも窒素原子、酸素原子、又は硫黄原子を含有する複素環化合物が特に好ましく、とりわけ窒素原子を含有する複素環化合物が好ましい。もちろんこうした複素環化合物は、更に金属に配位可能な官能基をも有するものであってもよい。更に金属に配位可能な官能基をも有する複素環化合物は、より高いパターン密着性を与える点で好ましい。

【0017】配位構造含有化合物の中でも硬化性樹脂組成物中の成分と反応し、これらの化合物が次の工程で形成される樹脂基材表面に強固に保持される点から、イミダゾール、2-メチルイミダゾール、2-エチル-4-

6

メチルイミダゾール、2-メルカプトメチルベンゾイミダゾール、2-エチルイミダゾール-4-ジチオカルボン酸、2-メチルイミダゾール-4-カルボン酸、1-(2-アミノエチル)-2-メチルイミダゾール、1-(2-シアノエチル)-2-メチルイミダゾール、2-フェニル-4, 5-ジヒドロキシメチルイミダゾール、ベンゾイミダゾール、2-エチル-4-チオカルバモイルイミダゾール等のイミダゾール類；ピラゾール、3-アミノ-4-シアノピラゾール等のピラゾール類；1, 2, 4-トリアゾール、2-アミノ-1, 2, 4-トリアゾール、1, 2-ジアミノ-1, 2, 4-トリアゾール、1-メルカプト-1, 2, 4-トリアゾール等のトリアゾール類；2-アミノトリアジン、2, 4-ジアミノ-6-(6-(2-(2-メチル-1-イミダゾリル)エチル)トリアジン2, 4, 6-トリメルカプト-s-トリアジン-トリソディウムソルト等のトリアジン類；が好ましい例としてあげられる。

【0018】（工程B）ここでは、工程Aを経た成形体を硬化して、表面にイニシエータパターンを有する樹脂基材を得る。硬化の方法は、成形体の性質に応じて選択すればよい。例えば、熱硬化性樹脂組成物の成形体であれば加熱条件に成形体をおくことによって硬化すればよいし、電離放射線硬化性樹脂組成物の成形体であれば遠紫外線、紫外線、可視光線のような光や電子線などを照射することによって硬化すればよい。例えば、熱硬化性樹脂組成物の成形体を硬化する場合、硬化させるための温度は、通常30～400℃、好ましくは70～300℃、より好ましくは100～200℃で、硬化時間は、通常0.1～5時間、好ましくは0.5～3時間である。加熱の方法は特に制限されず、例えばオープンなどを用いて行えばよい。

【0019】硬化によって、成形体は完全に硬化され、表面にイニシエータパターンを有する樹脂基材となる。従来は、成形体を完全に硬化してなる樹脂基材上にイニシエータパターンを形成していた点で、本発明とは大きく異なる。完全には硬化されていない成形体表面にイニシエータパターンを形成した後に、成形体を硬化することで、樹脂基材表面に、めっき誘発物質が取り込まれ、めっき誘発物質と樹脂基材とが強固に結合されるため、その上に形成されるめっきとの密着性も高まる。本発明の方法によれば、樹脂基材表面を粗化してからイニシエータパターンを形成する必要がなく、樹脂基材のイニシエータパターン（金属パターン）との界面の平坦な樹脂基材が得られる。ここで平坦とは、表面粗さRaが200nm以下、好ましくは100nm以下、より好ましくは80nm以下であることをいう。尚、ここで表面粗さRaは、JIS B 0601の規定に基づいて算出される値である。

【0020】上述した配位構造含有化合物を用いた場合、工程Bにおける硬化時に成形体表面の架橋密度をよ

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り高めることができる。このため、次に詳述する、必要に応じて行う樹脂基材表面の酸化工程で、樹脂基材表面や樹脂基材のイニシエータパターンとの界面に生じる樹脂基材の荒れを抑えることができる。

【0021】この工程Bにおける硬化で、樹脂基材表面に脆い層が形成されたり、硬化雰囲気から汚染物質が付着することがある。そこで、これらを除く目的で、基材表面を酸化（工程B'）するのが好ましい。基材表面を酸化する方法に格別な制限はないが、基材表面を荒らさないことから、酸化性化合物の溶液を用いる方法や

10 気体媒質を用いる方法など基材表面に化学物質を接触させる方法が望ましい。

【0022】酸化性化合物としては、無機過酸化物や有機過酸化物など、酸化能を有する公知の酸化性化合物が使用できる。無機過酸化物としては過マンガン酸塩、無水クロム酸、重クロム酸塩、クロム酸塩、過硫酸塩、活性二酸化マンガ、四酸化オスミウム、過酸化水素、過

20 よう素酸塩、オゾンなどが挙げられ、有機過酸化物としてはジクミルパーオキサイド、オクタノイルパーオキサイド、m-クロロ過安息香酸、過酢酸などが挙げられる。酸化性化合物を用いて樹脂基材表面を酸化する方法に格別な制限はなく、例えば酸化性化合物を、必要に応じてこれらを溶解可能な媒質に溶解して液状とした後、硬化後の樹脂基材と接触させる方法など一般的な方法が

30 挙げられる。酸化性化合物を溶解するのに用いる媒質としては、中性水、NaOH水溶液などのアルカリ水溶液、硫酸水溶液などの酸性水溶液、エーテルや石油エーテルなどの中性有機溶媒、アセトンやメタノールなどの極性有機溶剤が例示される。酸化性化合物を樹脂基材表面に接触させる方法に格別な制限はなく、例えば樹脂基

40 材を酸化性化合物溶液に浸漬するディップ法、基材の表面に表面張力を利用して酸化性化合物溶液を乗せる液盛り法、酸化性化合物溶液を基材に噴霧するスプレー法などいかなる方法であっても良い。これらの酸化性化合物を樹脂基材表面に接触させる温度や時間は、過酸化物の濃度や種類、接触方法などを考慮して、任意に設定すれば良く、温度が通常10～250℃、好ましくは20～180℃で、時間が0.5～60分、好ましくは1分～30分である。この範囲の下限未満では硬化後、硬化によって生じた樹脂基材表面の脆い層や硬化雰囲気から付

50 着した汚染物質を除去が不充分であったり、この範囲の上限を超えると樹脂基材表面が脆くなったり、表面の平滑性が損なわれる場合がある。

【0023】酸化性化合物を樹脂基材表面に接触させた後、酸化性化合物を除去するため、通常、樹脂基材を水で洗浄する。水だけでは洗浄しきれない物質が基材に付着する場合、その物質を溶解可能な洗浄液で更に洗浄したり、他の化合物と接触させて水に可溶な物質にしてから水で洗浄することもできる。例えば、過マンガン酸カリウム水溶液や過マンガン酸ナトリウム水溶液などのア

8

ルカリ性水溶液を樹脂基材と接触させた場合は、発生した二酸化マンガンの皮膜を除去する目的で、硫酸ヒドロキシアミンと硫酸との混合液などの酸性水溶液により中和還元処理する。

【0024】気体媒質を用いて酸化処理する方法として、逆スパッタリングやコロナ放電など媒質をラジカル化やイオン化させることが可能な公知のプラズマ処理が挙げられる。気体媒質としては大気、酸素、窒素、アルゴン、水、二硫化炭素、四塩化炭素などが例示される。媒質が処理温度雰囲気

10 で液状の場合には減圧下にて気化した後、酸化処理をし、媒質が処理温度雰囲気にて気体の場合はラジカル化やイオン化が可能な圧力に加圧した後、酸化処理をする。プラズマを樹脂基材表面に接触させる温度や時間は、ガスの種類や流量などを考慮して、任意に設定すれば良く、温度が通常10～250℃、好ましくは20～180℃で、時間が通常0.5～60分、好ましくは1分～30分である。

【0025】（工程C）ここでは、工程Bを経て得られた樹脂基材上にあるイニシエータパターン上に無電解め

20 っきを行う。通常、無電解めっきの前に、めっき触媒の付与や触媒の活性化といった処理を行う。めっき触媒は無電解めっき液中にてめっきの析出をさせる作用のある還元触媒となる金属化合物である。金属としては、Pd、Pt、Au、Ag、Ir、Os、Ru、Sn、Zn、Coなどが挙げられる。密着性を高めるためには、金属化合物として、還元によって金属の生成が可能な有機金属錯体や金属塩を用いるのが好ましく、具体的にはPdアミン錯体や硫酸パラジウム、塩化パラジウムなどが挙げられる。触媒付与と触媒の活性化の方法として

30 は、金属化合物を、水又はアルコール若しくはクロロホルムなどの有機溶媒に0.001～10重量%の濃度で溶解した液（必要に応じて酸、アルカリ、錯化剤、還元剤などを含有していてもよい）に浸漬して、めっき触媒を付与した後、金属を還元して触媒を活性化する方法などが挙げられる。イニシエータパターンにより多くの触媒が吸着されるが、イニシエータパターンのない部分に吸着した触媒を除去するのが望ましい。通常、不要の触媒を除去は、触媒付与後や触媒の活性化後に、水洗することにより行う。

【0026】このようにして樹脂基材のイニシエータパターン上に活性化された触媒を付与し、ついで無電解め

40 っき液と接触させて、無電解めっきを行う。無電解めっきに用いる無電解めっき液に格別な制限はないが、好ましくは公知の自己触媒型の無電解めっき液を用いる。無電解めっき液の具体例としては、次亜リン酸アンモニウム又は次亜リン酸、水素化硼素アンモニウムやヒドラジン、ホルマリンなどを還元剤とする無電解銅めっき液、次亜リン酸ナトリウムを還元剤とする無電解ニッケル

50 リンめっき液、ジメチルアミンボランを還元剤とする無電解ニッケルホウ素めっき液、無電解パラジウムめ

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9

き液、次亜リン酸ナトリウムを還元剤とする無電解パラジウム-リンめっき液、無電解金めっき液、無電解銀めっき液、次亜リン酸ナトリウムを還元剤とする無電解ニッケル-コバルト-リンめっき液等の無電解めっき液を用いることができる。無電解めっき後、基板表面を防錆剤と接触させて防錆処理をすることもできる。

【0027】無電解めっきを行い、樹脂基材表面に金属パターンを形成させた後、密着性を向上させるため、オープンなどを用いて樹脂基材を50～350℃、好ましくは80～250℃で、0.1～10時間、好ましくは0.1～5時間、加熱処理するのが好ましい（工程D）。このとき、窒素やアルゴンなどの不活性ガス雰囲気下で加熱するのが好ましい。更に必要に応じて、加熱時に、プレス板などで樹脂基材を加圧しても良い。

【0028】上述のような工程を経て、樹脂基材表面に無電解めっきを施すことにより、表面に金属パターンを有する本発明の樹脂部材が得られる。この樹脂部材は、例えば、半導体デバイス実装部品、各種パネル表示装置、ICカード、光デバイスに用いられるプリント配線基板として用いることができる。

【0029】

【実施例】以下に、実施例及び比較例を挙げて本発明を具体的に説明する。なお、実施例中、部及び％は、特に断りのない限り重量基準である。本実施例において行った評価方法は以下のとおりである。

(1) 分子量 (Mw, Mn)

トルエンを溶剤とするゲル・パーミエーション・クロマトグラフィー (GPC) によるポリスチレン換算値として測定した。

(2) 水素化率及び(無水)マレイン酸残基含有率
水素添加前の重合体中の不飽和結合のモル数に対する水素添加率(水素添加添加率)及び重合体中の総モノマー単位数に対する(無水)マレイン酸残基のモル数の割合(カルボキシル基含有率)は¹H-NMRスペクトルにより測定した。

(3) ガラス移転温度 (Tg)

示差走査熱量法 (DSC法) により測定した。

(4) 樹脂表面の粗さ

原子間力顕微鏡 (Digital Instrument 製、Nanoscope 3a) にてSi単結晶短冊型カンチレバー (バネ定数=20N/m、長さ125μm) を使用し大気中タッピングモードで表面平均粗さRaを測定して評価した。RaはJIS B 0601に定める算術平均粗さである。

(5) 密着性の評価

JIS C 5012 8.5に定めるめっき密着性の評価パターンを最外層に形成した多層基板を温度25℃相対湿度65%の雰囲気中に24時間放置した後、JIS C 5012 8.5に準じてめっき密着性の試験を実施して、めっき層の剥離や浮きの発生を目視にて観察

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した。剥離や浮きが観察されないものを良、剥離や浮きが観察されるものを不良とした。

(6) パターニング性の評価

配線幅30μm、配線間距離30μm、配線長5cmで50本の配線パターンを形成し、50本がいずれも形状に乱れの無いものを○、形状に乱れがあるが欠損の無いものを△、欠損のあるものを×として評価した。

【0030】実施例1

8-エチルーテトラシクロ [4.4.0.1².5.1⁷.1⁰] -ドデカ-3-エンを開環重合し、次いで水素添加反応を行い、数平均分子量 (Mn) = 31, 200、重量平均分子量 (Mw) = 55, 800、Tg=約140℃の水素化重合体を得た。得られたポリマーの水素化率は99%以上であった。得られた重合体100部、無水マレイン酸40部及びジクミルパーオキシド5部をt-ブチルベンゼン250部に溶解し、140℃で6時間反応を行った。得られた反応生成物溶液を100部のイソプロピルアルコール中に注ぎ、反応生成物を凝固させマレイン酸変性水素化重合体を得た。この変性水素化重合体の分子量はMn=33, 200、Mw=68, 300でTgは170℃であった。(無水)マレイン酸残基含有率は25モル%であった。

【0031】前記変性水素化重合体100部、ビスフェノールAビス(プロピレングリコールグリシジルエーテル)エーテル40部、2-[2-ヒドロキシ-3, 5-ビス(α, α-ジメチルベンジル)フェニル]ベンゾトリアゾール5部及び1-ベンジル-2-フェニルイミダゾール0.1部を、キシレン215部及びシクロペンタノン54部からなる混合溶剤に溶解させて、硬化性樹脂組成物のワニスを得た。

【0032】当該ワニスを、ダイコーターを用いて、300mm角の厚さ40μmのポリエチレンナフタレートフィルム(キャリアフィルム)に塗工し、その後、窒素オーブン中、120℃で10分間乾燥し、樹脂(硬化性樹脂組成物の成形体に相当)層の厚みが35μmのキャリアフィルム付きドライフィルムを得た。

【0033】一方、2-ジ-*n*-ブチルアミノ-4, 6-ジメルカプト-*s*-トリアジンの0.1%イソプロピルアルコール溶液を調製し、この溶液に配線幅及び配線間距離が50μm、導体厚みが18μmで表面がマイクロエッチング処理された内層回路を形成された厚さ0.8mmの両面銅張り基板(ガラスフィラー及びハロゲン不含エポキシ樹脂を含有するワニスをガラスクロスに含浸させて得られたコア材)を25℃で1分間浸漬し、次いで90℃で15分間、窒素置換されたオーブン中で乾燥させてプライマー層を形成させて、内層基板を得た。

【0034】前述の内層基板上に、前述のキャリアフィルム付きドライフィルムを、樹脂面が内側となるようにして両面銅張り基板両面に重ね合わせた。これを、一次

(7)

11

プレスとして耐熱ゴム製プレス板を上下に備えた真空ラミネータを用いて、200Paに減圧して、温度110℃、圧力0.5MPaで60秒間加熱圧着した。次いで、二次プレスとして金属製プレス板で覆われた耐熱ゴム製プレス板を上下に備えた真空ラミネータを用いて、200Paに減圧して、温度140℃、1.0MPaで60秒間、加熱圧着して硬化性樹脂組成物の成形体を積層させた。

【0035】前述の硬化性樹脂組成物の成形体を積層させた基板からポリエチレンナフタレートフィルムのみを剥がした。硬化性樹脂組成物の成形体の表面粗さを評価したところ、Raは14nmであった。次いでこの基板に積層された硬化性樹脂組成物の成形体表面に、めっき誘発物質として1-(2-アミノエチル)-2-メチルイミダゾールが0.3%になるように調製した水溶液を、インクジェット装置を用いて所望の配線パターンに描画し、成形体表面に無電解めっき用イニシエータパターンを形成した。これを170℃の窒素オーブン中に60分間放置して、硬化性樹脂組成物の成形体を硬化させ、内層基板上に樹脂基材である電気絶縁層を形成して、積層板を得た。尚、この積層板の表面には、イニシエータパターンが形成されている。得られた積層板の、絶縁層部分に、UV-YAGレーザ第3高調波を用いて直径30μmの層間接続のビアホールを形成しビアホールつき多層基板を得た。

【0036】めっき前処理として、上述のビアホールつき多層基板を過マンガン酸濃度60g/リットル、水酸化ナトリウム濃度28g/リットルになるように調整した80℃の水溶液に10分間揺動浸漬し、表面を酸化させた。次いで、基板を水槽に1分間揺動浸漬し、更に別の水槽に1分間揺動浸漬することにより、基板を水洗した。続いて硫酸ヒドロキシルアミン濃度170g/リットル、硫酸80g/リットルになるように調整した25℃の水溶液に、基板を5分間浸漬し、中和還元処理をした後、水洗をし、窒素を吹き付けて水を除去した。

【0037】めっき触媒付与のため、水洗後の多層基板をアクチベータMAT-1-A（上村工業株式会社製）が200ml/リットル、アクチベータMAT-1-B（上村工業株式会社製）が30ml/リットル、水酸化ナトリウムが1g/リットルになるように調整した60℃のPd塩含有めっき触媒溶液に5分間浸漬した。次いで、触媒活性化のため、上述と同じ方法で基板を水洗した後、レデューサーMRD-2-A（上村工業株式会社製）が18ml/リットル、レデューサーMRD-2-C（上村工業株式会社製）が60ml/リットルになるように調整した溶液に35℃で、5分間、浸漬し、めっき触媒を還元処理した。このようにしてめっき触媒を吸着させ、得られた多層基板の最外絶縁層表面の粗さを評価したところ、パターンを描画した部分のRaは32nm、パターンを描画していない部分のRaは29nm

12

と、ほぼ同じRa値であった。

【0038】こうして得られた多層基板を、スルカップPRX-1-A（上村工業株式会社製）が150ml/リットル、スルカップPRX-1-B（上村工業株式会社製）が100ml/リットル、スルカップPRX-1-C（上村工業株式会社製）が20ml/リットルになるように調整した25℃の無電解めっき液に空気を吹き込みながら、15分間浸漬して無電解めっき処理し、上述と同様に水洗して、所望のパターン状に金属パターンが形成された多層基板を得た。次いで、金属パターンの厚みを増す目的で、スルカップELC-SP-A（上村工業株式会社製）が80ml/リットル、スルカップELC-SP-B（上村工業株式会社製）が20ml/リットル、スルカップELC-SP-C（上村工業株式会社製）が80ml/リットル、スルカップELC-SP-D（上村工業株式会社製）が20ml/リットルになるように調整した60℃の高速無電解めっき液に空気を吹き込みながら、5時間浸漬して無電解めっき処理し厚さ18μmの先に形成した金属パターン状にさらに金属を重ねた。更に上述と同様に水洗して、所望のパターン状に金属パターンが形成された多層基板を得た。次いで、AT-21（上村工業株式会社製）が10ml/リットルになるよう調整した防錆溶液に25℃、1分間浸漬し、更に上述と同じ方法で水洗した後、乾燥し、防錆処理を施した。

【0039】この防錆処理が施された多層基板を、窒素雰囲気下のオーブン中にて170℃で30分間放置して、加熱処理して前記無電解銅めっきにより形成された金属パターンを両面に有する多層回路基板を得た。得られた多層回路基板のパターンが無い部分の電気絶縁層（樹脂基材）表面の粗さを評価したところRaは31nmであった。得られた多層回路基板のパターニング性の評価及びめっき密着性の評価を行った。評価結果を表1に示す。

【0040】実施例2

1-(2-アミノエチル)-2-メチルイミダゾールが0.3%になるように調整した水溶液100部に、チキソトロピー性を付与する目的でAEROJILRY200（日本アエロジル株式会社製）を15部添加して、デイズルバーを用いて周速10m/秒で混合分散させた分散溶液を調整した。実施例1の1-(2-アミノエチル)-2-メチルイミダゾールが0.3%になるように調整した水溶液に代えて、この分散溶液を用い、イニシエータパターンに描画するために用いる装置をスクリーン印刷装置に変えたこと以外は実施例1と同様に実施した。めっき前処理を実施した後の最外絶縁層表面の粗さを評価したところ、イニシエータパターンを印刷した部分のRaは58nm、印刷していない部分のRaは32nmと、ほぼ同じRa値であった。得られた多層回路基板のパターンが無い部分の絶縁層表面の粗さを評価したと

(8)

13

ころRaは33nmであった。得られた多層回路基板のパターン密着性、パターンニング性の評価結果を表1に示す。

【0041】比較例1

実施例1にて過マンガン酸処理しない以外は実施例1と同様ににして多層回路基板を得た。めっき前処理を実施した後の最外絶縁層表面の粗さを評価したところ、パターンを描画してある部分のRaは31nm、パターンを*

14

*描画していない部分のRaは26nmであった。得られた多層回路基板のパターンが無い部分の絶縁層表面の粗さを評価したところRaは31nmであった。得られた多層回路基板のパターン密着性、パターンニング性の評価結果を表1に示す。

【0042】

【表1】

(表 1)

実施例	密着性	パターンニング性
実施例1	良	○
実施例2	良	○
比較例1	不良	△

【0043】以上の結果から、硬化前の硬化性樹脂成形体表面にめっき誘発物質からなるイニシエータパターンを形成すると、硬化後の樹脂基材表面にイニシエータパターンを形成した場合と比べ、優れた密着性の得られることが判った。特に本発明の部分めっき法は、樹脂基材

20

表面を粗化する必要がなく、金属パターンとの界面にある樹脂基材の表面粗さの小さい樹脂部材が得られる。このため、粗化された樹脂基材を用いることの問題が指摘されている回路基板の製造にも適している。